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Organophosphorus zwitterions engaged in a conjugated macrocycle on fullerene

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Organophosphorus zwitterions are one of the most important but elusive intermediates for carbon-carbon bond formation in synthetic chemistry and biology. However, a lack of isolated examples due to their lability has hampered in-depth understanding of structures and their reaction mechanisms. In this study, we crystallographically reveal the solid-state structure of a phosha-Michael adduct engaged in a cage-opened C₆₀ skeleton, which is formed as a kinetic product. This compound exhibits dark brown colour in solution with an intense absorption band that extends to 1000 nm, reflecting intramolecular charge transfer transitions. From the 1,2-dicarbonyl moiety on the conjugated orifice, β-oxo-phosphorus ylide is formed as a thermodynamic product. The reaction mechanism that has long been disputed is examined by experimental and theoretical studies, showing a pathway which includes an S_N2 reaction as a key step instead of the hitherto considered carbene pathway.

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Owing to large synthetic utility of phosphorus ylides demonstrated by Wittig in 1953^{1,2} as well as the discovery of the first naturally occurring compound bearing a C–P bond in 1959³, organophosphorus compounds have received growing attention⁴. Currently, their unique structural and electronic properties are often utilized in functionalized π -conjugated motifs⁵. Importantly, trivalent phosphorus compounds possess characteristics both of nucleophilicity and leaving-group ability, which allow them to proceed a variety of catalytic reactions commenced with their conjugate addition to α , β -unsaturated carbonyl compounds, leading to numerous biologically and synthetically valuable materials⁶. Even though zwitterionic forms of betaines have long been postulated as elusive key intermediates in such phospho-Michael addition⁷, their isolation, structural characterization, and mechanistic aspects have been still limited and remain formidable challenging issue^{8,9}. Another long-felt but unsolved issue in phosphorous chemistry is a mechanism for forming β -oxo-phosphorous ylides from 1,2-dicarbonyl compounds, in which a carbene intermediate has been proposed to be formed from Kukhtin–Ramirez adduct without definitive evidence^{10–12}.

Herein, we report isolation and crystallographic characterization of phospho-Michael adduct (1-phosphonium-5-oxabetaine) and β -oxo-phosphorus ylide embedded in a conjugated macrocyclic orifice on fullerene C₆₀. The characteristic features of C₆₀, i.e., excellent electron-accepting ability and π -conjugation along with the entire sphere, enabled the addition of phosphorus nucleophiles^{13–15} and stabilize reactive zwitterionic species. The mechanistic studies disclosed a rational pathway for forming β -oxo-phosphorus ylide, which is different from hitherto considered carbene pathway, as supported both experimentally and theoretically. These spherically π -conjugated zwitterions demonstrate significant change in electronic structures displaying an intense NIR absorption band up to 1000 nm with drastically elevated HOMO level.

Results and discussion

Synthesis. As a conjugate macrocyclic orifice on the C₆₀ cage, we made a choice of open-cage derivative **1** having α , β -unsaturated carbonyl and 1,2-dicarbonyl moieties (Fig. 1a). The reaction of **1** with the smallest alkyl phosphine (PMe₃) was examined in *o*-dichlorobenzene-*d*₄ (ODCB-*d*₄) at room temperature. The addition of 1 equiv. PMe₃ (1.0 M in toluene) to **1** in a sealed vessel caused the rapid change in color from reddish orange to dark brown. The APCI (atmospheric-pressure chemical ionization) mass spectrum of this solution clearly showed a molecular ion peak at m/z 1211.2073 ($[1 + \text{PMe}_3 + \text{H}]^+$), which is identical to a betaine derivative. The NMR spectra showed the quantitative conversion of **1** into the sole product (**2**) bearing a PMe₃ substituent with a broad doublet ¹H signal (δ + 3.19 ppm, ³J_{PH} = 12.0 Hz) and a singlet ³¹P signal (δ + 37.1 ppm) (Fig. 1b). The ³¹P signal observed at δ + 37.3 ppm corresponds to H₂O@2 formed via spontaneous encapsulation of a water molecule. Once the reaction system was opened into air, the solution turned back to the original color of **1** within a few minutes. The structure of **2** was unambiguously determined by the single-crystal X-ray analysis (vide infra). This is the first example to characterize 1-phosphonium-5-oxabetaine engaged in a polycyclic aromatic compound. Among five possible sites C(1)–C(5) for the phospho-Michael addition (Fig. 1a), the reactions at C(1) and C(5) should be sterically prohibited due to the bulky aryl substituents. According to DFT calculations at the M06-2X/6-31 G(d,p) level of theory in which *t*-butyl groups were replaced with hydrogen atoms, the energy required for forming a betaine derivative is rather small for **2'** (Ar = 2-pyridyl) obtained by the reaction at C(2) ($\Delta G^\ddagger$ + 11.9 kcal/mol at 298 K) compared to those at C(3) and C(4) ($\Delta G^\ddagger$ + 21.0 and +21.9 kcal/mol, respectively) (Supplementary Figs. 38, 39).

Notably, further addition of PMe₃ resulted in less considerable NMR spectral change, demonstrating that **1** does not undergo any multiple addition of phosphine (Fig. 1b). However, by

Fig. 1 Synthesis of 1-phosphonium-5-oxabetaine. **a** Reaction of **1** with PMe₃. **b** ¹H (500 MHz) and ³¹P (202 MHz) NMR spectra (ODCB-*d*₄).

Table 1 Synthesis of β -oxo-phosphorus ylides **3a–e**.

Entry	PR ₃ (equiv.)		Temp. (°C)	Time (h)	3 (%)	4 (%)
1 ^a	PMe ₃ ^c	(10)	60	1	44 (3a)	42
2 ^b	PCy ₃	(10)	150	0.25	48 (3b)	8
3 ^a	P(NMe ₃) ₂	(10)	150	4	82 (3c)	—
4 ^b	PPh ₃	(20)	150	4	72 (3d)	3
5 ^b	dppf ^d	(10)	150	5	49 (3e)	12

^a**1**: ca. 9 mM.
^b**1**: ca. 30 mM.
^c1.0 M in toluene.
^ddppf: 1,1'-bis(diphenylphosphino)ferrocene.

Fig. 2 Single-crystal X-ray structures. **a** Structure of **fA-2**. **b** Packing mode of **2**. **c** Structure of **3d**. **d** Selected bond lengths (units in Å). Thermal ellipsoids are shown in 50% probability. The encapsulated molecules, solvent molecules, aryl groups, and another independent molecule (**fC-2**) are omitted for clarity. The bond lengths shown with gray color belong to **fC-2**.

heating the 1:2 reaction mixture at 150 °C for 15 min, the solution color changed to greenish brown with the complete consumption of **2** equiv. PMe₃, affording O=PMe₃ and a new compound bearing a PMe₃ substituent (**3a**) in a 1:1 ratio (Fig. 1b). The ¹³C NMR spectrum of **3a** (CDCl₃, 126 MHz) showed a new doublet signal corresponding to a fullerenyl *sp*³-carbon atom directly

bound to a phosphorus atom ($\delta + 75.7$ ppm, ¹J_{CP} 122.6 Hz) together with three carbonyl carbon signals including a doublet one at $\delta + 188.63$ ppm weakly coupled with ³¹P (²J_{CP} = 13.2 Hz). These data convinced us of the structure for **3a** to be a β -oxo-phosphorus ylide^{16,17} formed by the reaction at the 1,2-dicarbonyl moiety in **1**.

Fig. 3 Plausible mechanism. The ΔG (kcal/mol at 298 K) values were calculated at the M06-2X/6-31 G(d,p) level of theory.

Subsequently, we performed the reaction using several phosphines, which gave **3a–e** in moderate to high yields (Table 1). Increased concentration of **1** was quite effective for lower-nucleophilic phosphines¹⁸, PPh_3 and dppf. Contrary to **3b–e** bearing a PR_3 substituent with a cone angle¹⁹ exceeding 140° (PCy_3 : 170° , $P(NMe_2)_3$: 157° , and PPh_3 : 145°), **3a** (PMe_3 : 118°) was significantly transformed into methylene derivative **4** during the reaction and the workup process. The hydrolysis²⁰ of **3a** in ODCB at $150^\circ C$ for 1 day resulted in quantitative conversion into **4**, whereas **3d** was not considerably hydrolyzed (13%) even after

6 days. These results are indicative of the steric protection for phosphorus centers in **3b–e**.

Crystallography. To our delight, the black platelet single crystals of **2** were obtained by slow diffusion of PMe_3 /toluene to a $CHCl_3$ solution of **1** under argon atmosphere at $5^\circ C$. The X-ray diffraction analysis revealed that an asymmetric unit accommodates a racemate including two enantiomeric isomers $^fC-2$ and $^fA-2$ arranged as two crystallographically independent molecules

Fig. 4 Electrochemical and absorption properties. **a** Cyclic voltammograms of **1** and **3c** (1 mM in ODCB, 0.10 M *n*-Bu₄N⁺BF₄⁻, 100 mV/s). **b** UV-vis-NIR absorption spectra of **1**, **2**, and **3c** (50 μ M in toluene). The inset shows an expanded view of long wavelength region with calculated oscillator strengths, which were plotted at corresponding transition energies calibrated by a factor of 0.72³² (TD CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d)).

(nomenclature based on criteria stated by Diederich^{21,22}). Interestingly, a unit of the racemate is assembled with another one as a tetrahedral configuration via heterochiral recognition (Fig. 2a, b). The driving force for this self-assembly should be attributed to the intermolecular electrostatic attraction between ⁺PMe₃ and C–O[−] moieties (3.646(4) and 3.668(4) Å for P...O) and thus the reactive sites (phosphonium betaine) were fully covered with the four fullerene cages in total. From the bond lengths, the structure of **2** can be rationalized by describing a resonance hybrid consisting of 1-phosphonium-5-oxabetaïne and 1-phosphonium-3-carbabetaine as major contributing forms (Fig. 2d). For β -oxo-phosphorus ylide **3d**, the black block-shaped single crystals were grown from a CH₂Cl₂/hexane solution. As shown in Fig. 2c, the phosphorus ylide was formed at the 1,2-dicarbonyl moiety in **1**. The bond length of the C–P bond in **3d** is 1.739(3) Å, which is explicitly longer than that for PPh₃P=CH₂ (1.66 Å)²³. This is suggestive of the charge delocalization along with C–C–O and other C₆₀ moieties (Fig. 2d), being consistent with the natural population and Wiberg bond order analyses (Supplementary Note 3).

Mechanism. To verify the possible pathway for providing **3a** from **1** and PMe₃, we performed DFT calculations (M06-2X/6-31 G(d,p), 298 K) (Fig. 3; Supplementary Notes 1 and 2). The first step is the nucleophilic attack of PMe₃ to the carbonyl group in **1'** (Ar = 2-pyridyl) to give **INT1** via **TS1** ($\Delta G^\ddagger + 27.8$ kcal/mol), which is slightly lower than that of the phospho-Brook rearrangement (+28.5 kcal/mol)²⁴. Even though the formation of carbene intermediates has been addressed as the second step²⁵, the calculated energy of **INTa** (+59.2 kcal/mol) obviously excludes such possibility as well as pentavalent phosphorus intermediate **INTb** (+27.1 kcal/mol)^{26,27}. This results are in line with our experimental observation that carbene scavengers, e.g., terminal olefins, could not trap any species. Since the hydrolysis of an **INT1**-type intermediate has been reported by Gan and co-workers²⁸, we computed the process toward **INT2**, showing $\Delta G^\ddagger + 15.3$ kcal/mol (**TS2**). The further transformation into **INT3** in an S_N2 fashion²⁹ with the loss of O=PMe₃ needs $\Delta G^\ddagger + 11.0$ kcal/mol (**TS3**), which is substantially lower than alternative pathways **TSa–c**. In this step, we adopted A[−] as a possible counter anion^{30,31}, which was observed in

the crude mixture of our reactions (Table 1, entry 1) by APCI MS. Finally, deprotonation of **INT3** proceeds to furnish desired **3a'** via **TS4** ($\Delta G^\ddagger + 5.9$ kcal/mol).

Electronic properties. The cyclic voltammogram of **3c** showed the reversible first and second reduction waves at E_{red} −1.33 and −1.73 V, which are close to the second and third ones for **1** at E_{red} −1.39 and −1.77 V, respectively (Fig. 4a). Thus, **3c** has the electron configuration similar to the monoanionic state of **1**, further suggesting that the anionic charge, which stems from the C[−]–P⁺ bond, is effectively delocalized on the C₆₀ skeleton. Since the HOMO is mainly localized on the C[−]–P⁺ bond (Supplementary Fig. 53), a single electron oxidation of **3c** at $E_{pa,ox} + 0.56$ V is supposed to generate a radical cation with a C[•]–P⁺ character. As shown in Figs. 2 and 3c, **4b** exhibited intense absorption bands at NIR region, which tail to 1000 and 900 nm, respectively. Whereas the HOMO and LUMO of **1** are delocalized over the entire C₆₀ skeleton, **2** and **3c** show the HOMO localized at the betaine and ylide moieties, respectively. Thereby, intramolecular charge transfer transitions (HOMO $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO + 1) with large oscillator strengths ($f = 0.0192$ at 897 nm for **2** and $f = 0.0334$ at 680 nm for **3c**) should contribute to the observed intense absorption with remarkable bathochromic shift up to 300 nm relative to **1** (TD CAM-B3LYP/6-31G(d)//B3LYP/6-31G(d)) (Supplementary Note 4).

In summary, by the reaction of phosphines with a conjugated macrocycle on **1**, betaine and ylide derivatives were found to be formed as kinetic and thermodynamic products, respectively. The first phospho-Michael adduct engaged in a polycyclic aromatic compound (**2**) showed a self-assembled structure in the solid state. The rational reaction mechanism was proposed for forming ylide **3** from 1,2-dicarbonyl compound **1** based on experimental and computational studies, suggestive of the S_N2 reaction as a key step instead of hitherto considered carbene pathway²⁵. Importantly, the introduction of the PR₃ moiety drastically changes the properties of the π -skeleton, resulting in intense NIR absorption with elevated HOMO level. These findings are expected to promote further explorations of phosphorus-bearing π -conjugated materials.

Methods

General. All reactions were carried out under Ar atmosphere. Unless otherwise noted, materials purchased from commercial suppliers were used without further purification. Note that all the compounds shown herein encapsulate a water molecule inside their cages with an occupation level of 10–70% at room temperature. For the simplification, the encapsulated water molecules are omitted for clarity in chemical structures for all figures. Compound **1** was synthesized according to the literature³³. The detailed procedures and the data required for characterization are provided in the Supplementary Methods.

Synthesis of 2. Compound **1** (10.0 mg) was placed into a Schlenk-type NMR tube and degassed through three vacuum-Ar cycles. Distilled ODCB-*d*₄ (0.650 mL, 13.6 mM) and then PMe₃ (1.0 M in toluene, 8.80 μ L, 1.0 equiv.) were added at room temperature. The quantitative conversion into **2** was confirmed by NMR and mass analyses.

Synthesis of 3. The typical synthetic procedure of **3a** was shown. Other β -oxo-phosphorus ylides **3b–e** were synthesized by the procedure shown in the Supplementary Information. Compound **1** was placed into a Schlenk tube and degassed through three vacuum-Ar cycles. ODCB (1.0 mL, 8.8 mM) and then PMe₃ (1.0 M in toluene, 88.1 μ L, 10 equiv.) were added to the tube. The resulting mixture was heated at 60 °C for 1 h. After reaction, residual PMe₃ and its oxide were removed under reduced pressure. The chromatographic purification by silica gel (CS₂/EtOAc (10:1 to 4:1)) gave **3a** (4.63 mg) in 44% isolated yield as black powder.

Preparation of single crystals. Since **2** is moisture- and air-sensitive, the crystals were grown under inert conditions. A micro tube containing **1** (ca. 0.5 mg) was capped with a rubber septum and degassed through vacuum-Ar cycles. After ca. 0.2 mL of CHCl₃ was added to dissolve **1**, toluene was slowly added to make a thin-layer. To the tube, an excessive amount of PMe₃ in toluene was added in one portion at room temperature. The resulting solution was kept at 5 °C overnight. The black platelet single crystals were formed onto the bottom surface. The single crystals of **3d** were obtained from a CH₂Cl₂/hexane solution by slow evaporation at room temperature.

Electrochemical analysis. Cyclic voltammetry was conducted using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgNO₃ reference electrode. The measurements were carried out under N₂ atmosphere using ODCB solutions of 1.0 mM samples and 0.10 M tetrabutylammonium tetrafluoroborate (*n*-Bu₄N·BF₄) as a supporting electrolyte. The redox potentials were calibrated with ferrocene used as an internal standard, which was added after each measurement.

Data availability

Detailed experimental procedures, characterization data (Supplementary Figs. 1–37), and computational results (Supplementary Figs. 38–53 and Supplementary Tables 1–59) are provided in the Supplementary Information. CCDC 1988945 (**2**) and 1988944 (**3d**) contain the supplementary crystallographic data for this paper (Supplementary Data 1 and 2). These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Author contributions

Y.M. conceived and designed the total project. Y.H. and S.O. conducted all experiments. Y.H. performed theoretical calculations and crystallographic analyses. Y.H. wrote the manuscript and discussed the results with all authors.

Competing interests

The authors declare no competing interests.

Additional information

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